

## PREFACE

*"The process of scientific discovery is, in effect, a continual flight from wonder."*

*Albert Einstein*

Contemporary laser research involves the development of spectroscopic techniques to understand the microscopic structural aspects of a simple molecular system in chemical and materials to more complex biological systems such as cells. In particular, Raman spectroscopy, which provides bond specific information, has attracted considerable attention. Further with the advent of femtosecond (fs) laser, the recent trend in the field of fs chemistry is to develop nonlinear Raman techniques that allow one to acquire vibrational structural information with both fs temporal resolution as well as good spectral resolution. Among many advanced nonlinear Raman techniques, the development of fs Stimulated Raman scattering (SRS) has gathered momentum in the recent decade due to its ability to (1) provide vibrational structural information of various system including fluorescent molecules with good signal to noise ratio and (2) circumvent the limitation imposed on the spectral resolution ( $\Delta\nu$ ) by the necessary pulse durations ( $\Delta\tau$ , fs) according to the energy-time uncertainty principle ( $\Delta\nu \times \Delta\tau = K$ , where 'K' is a constant that depends on the pulse shape) unlike in the case of fs normal resonance Raman spectroscopy.

We have developed a technique named “*Ultrafast Raman loss spectroscopy (URLS)*” that is analogous to SRS, but is more advantageous as compared to SRS and has the potential to be an alternative if not competitive tool as a vibrational structure elucidating technique. The concept and the design of this novel technique, URLS, form the core of the thesis entitled “*Ultrafast Raman Loss Spectroscopy (URLS)*”.

**Chapter 1** lays the theoretical groundwork for ultra-short pulses and nonlinear spectroscopy which forms the heart of URLS. It presents a detailed discussion on the basis behind the elementary experimental problems associated with the ultra-short laser pulses when they travel through a medium, the characterization of these ultra-short pulses as well as various non-linear phenomena induced within a medium due to the propagation of these pulses.

**Chapter 2** focuses on the concept of SRS which resulted into the foundation of URLS. It illustrates the theoretical as well as the experimental aspects of SRS and demonstrates the sensitivity of SRS over normal Raman spectroscopy.

**Chapter 3** introduces the conceptual and the technical basis which ensued into the development of URLS while **Chapter 4** demonstrates its application and efficiency over its analogue SRS. URLS involves the interaction of two laser sources, *viz.* a picosecond (ps) pulse and a fs white light (WL), with a sample leading to the generation of loss signal on the higher energy (blue) side with respect to the

wavelength of the ps pulse unlike the gain signal observed on the lower energy (red) side in SRS. These loss signals are at least 1.5 times more intense than SRS signals. Also, the very prerequisite of the experimental protocol for signal detection to be on the higher energy side by design eliminates the interference from fluorescence, which appears on the red side. Thus, the rapid data acquisition, 100% natural fluorescence rejection and experimental ease ascertain “*Ultrafast Raman Loss Spectroscopy (URLS)*” as a unique valuable structure determining technique.

Further, the effect of resonance on the line shape of the URLS signal has been studied which forms the subject of discussion in **Chapter 5**. The objective of the study is to verify whether the variation of resonance Raman line shapes in URLS could provide an understanding of the mode specific response on ultrafast excitation. It is found that the URLS signal’s line shape is mode dependent and can provide information similar to Raman excitation profile (REP) in the normal Raman studies. This information can have impact on the study of various dynamical process involving vibrational modes like structural dynamics and coherent control.

**Chapter 6** demonstrates the application of URLS as a structure elucidating technique for monitoring ultrafast structural and reaction dynamics in both chemical and biological systems using  $\alpha$ -terthiophene (3T) as the model system. The objective is to understand the mechanism of the molecular structure dependent electronic relaxation

of the first singlet excited state,  $S_1$ , of  $\alpha$ -terthiophene using fs URLS. The URLS data along with the *ab-initio* calculations indicate that the electronic transition is associated with a structural rearrangement from a non-planar to a planar configuration in the singlet manifold along the ring deformation co-ordinate. The experimental findings suggest that the singlet state decays exponentially with a decay time constant ( $\tau_{1/e}$ ) of about 145 ps and this decay could be assigned to the intersystem crossing (ISC) pathway from the relaxed  $S_1$  state to the vibrationally hot triplet state,  $T_1^*$ .

Lastly, **Chapter 7** summarizes the entire thesis and presents some possible future prospects for URLS. Considering the advantages of URLS, it is proposed that URLS can be exploited [1] to determine the structure of any fluorescent/non-fluorescent condensed materials and biological systems with a very good spectral resolution (10-40  $\text{cm}^{-1}$ ); [2] to obtain the vibrational signature of weak Raman scattering molecules and vibrational modes with relatively small Raman cross-section owing to its high detection sensitivity with good signal to noise ratio; [3] for performing fs time-resolved study by introducing an additional fs pulse for photo-excitation of the molecule and using URLS to probe the excited state dynamics with good temporal (fs) and spectral (10-40  $\text{cm}^{-1}$ ) resolution; and lastly, [4] the high chemical selectivity of URLS and the fact that the signal is generated only within the focal volume of the lasers where all the beams overlap can be utilized for developing this method into a microscopy for labeled-free effective vibrational study of biological samples.

Consequently, it is hoped that this technique, “*Ultrafast Raman Loss Spectroscopy (URLS)*”, would be a suitable alternative to other nonlinear Raman methods like coherent anti-Stokes Raman spectroscopy (CARS) that has made major inroads into biology, medicine and materials.

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